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By M. J. Ferrante and R. V. Mrazek



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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere	J	joule
cal	calorie	K	kelvin
cal/(mol·K)	calorie per mole per kelvin	kcal/mol	kilocalorie per mole
cm ³	cubic centimeter	μK	microkelvin
deg	degree	μV	microvolt
g	gram	pct	percent
g/cm ³	gram per cubic centimeter	wt pct	weight percent
h	hour		

HIGH-TEMPERATURE RELATIVE ENTHALPIES OF V_2O_5

By M. J. Ferrante¹ and R. V. Mrazek²

ABSTRACT

Relative enthalpies of V_2O_5 from 298.15 to 1,101.0 K were measured at the Bureau of Mines to provide data needed for the advancement of mineral technology. Enthalpies were measured with a copper-block calorimeter. A sharp melting point was found at 951 K, with $\Delta_m^\circ = 15.690$ kcal/mol for the standard enthalpy of melting. Tabulated values are given at selected temperature increments between 298.15 and 1,500 K for the standard relative enthalpy ($H^\circ - H_{298}^\circ$), heat capacity (C_p°), entropy (S°), and Gibbs energy function $[-(G^\circ - H_{298}^\circ)/T]$. Standard relative enthalpies are also given in equation form and combined with data from the literature to derive values of standard enthalpies of formation and Gibbs energies of formation.

INTRODUCTION

Relative enthalpies of high-purity divanadium pentoxide (V_2O_5) were measured at the Bureau of Mines to provide reliable data for the advancement of mineral technology. Previous measurements of relative enthalpies for V_2O_5 by Cook (1)³ and Slyusar (2) were scattered and diverged from each other. The difference between them was 6.9 pct at 500 K for solid V_2O_5 and 2.7 pct at 1,000 K for the liquid. The data of Cook could not be smoothly merged with the low-temperature heat capacities measured by Anderson (3) or by Sukhovei (4); however, relative enthalpies of Slyusar could be merged with the data of Sukhovei. These differences were resolved by the highly reliable measurements of the present investigation, which resulted in an average deviation of 0.02 pct between the experimental and smoothed enthalpies, and which were smoothly merged with the low-temperature data of Sukhovei.

Unless designated otherwise, V_2O_5 refers to the orthorhombic crystal form. This is the stable phase in the temperature range of 0 to the melting point at 951 K.

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³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

MATERIALS

The V_2O_5 used in this investigation was prepared by treating powdered V_2O_5 to remove a sodium impurity of 0.4 pct sodium monoxide (Na_2O). Treatment consisted of digesting 50-g lots in 200 mL of 0.3N hydrochloric acid (HCl) for 2 h. The acid digestion was repeated, and the V_2O_5 was then digested six times in boiling distilled water. After each digestion, the hot mixture was centrifuged to remove the supernatant liquid. The V_2O_5 was dried at 393 K, ground to a powder, blended

thoroughly, and then calcined at 823 K for 16 h in a platinum dish. Chemical analysis showed the sodium impurity level to be reduced to less than 0.01 pct. The X-ray diffraction pattern matched the pattern for orthorhombic V_2O_5 given on the Powder Diffraction File card 9-387. Optical emission spectroscopy showed the total metallic impurities to be less than 0.03 wt pct. The absolute impurity of the V_2O_5 is considered to be greater than 99.97 pct.

EXPERIMENTAL WORK AND RESULTS

Enthalpies above 298.15 K were measured by drop calorimetry. The calorimeter has a copper block enclosed in an isothermal jacket. This calorimeter has a potentiometric system capable of detecting a change of $\pm 50 \mu K$ or $\pm 0.02 \mu V$. Detailed descriptions of the construction and operation of the calorimeter were given by Ferrante (5).

Relative enthalpies are expressed in terms of the thermochemical calorie where $1 \text{ cal} = 4.1840 \text{ J}$. Before and after a series of enthalpy measurements for a substance, the calorimeter was calibrated electrically and the entire system was checked for accuracy by measuring the enthalpy of periclase (MgO). These MgO measurements agreed to within 0.1 pct with the values reported by Victor (6) from 298 to 1,200 K. The temperature of a sample in the furnace was measured with a platinum versus platinum-10 wt pct rhodium thermocouple, which was frequently calibrated against the melting point of pure gold. The furnace used to heat the sample contained a cylindrical silver heat sink that provided a near isothermal zone for the sample and the thermocouple. The temperature (T) is in kelvins as defined by the International Temperature Scale of 1968 (7).

Experimental measurements of relative enthalpies were made with V_2O_5 sealed in

a capsule of platinum-10 wt pct rhodium (Pt-10 wt pct Rh). The V_2O_5 was loaded into the capsule in air, heated at 380 K for 0.5 h, and then heated at 675 K for 19 h. After the capsule was evacuated and backfilled with approximately 1 atm of ultra-high-purity helium, its neck was squeezed gastight. The neck of the capsule was then sealed by arc-welding with a nonconsumable electrode while under a stream of inert gases. A sample mass of 7.75139 g of V_2O_5 (vacuum corrected) was sealed in 9.78665 g of Pt-10 wt pct Rh. This amount of Pt-10 wt pct Rh contributed about 19 pct of the total measured enthalpy from 400 K to below the melting point at 951 K, and approximately 12 pct thereafter.

The capsule had an internal volume of 4.76 cm^3 . The volume of the V_2O_5 in the capsule was 2.30 cm^3 , based on the density of 3.372 g/cm^3 . The molecular weight of 181.880 for V_2O_5 conforms to the 1981 Table of Atomic Weights (8).

The results of experimental measurements are listed in table 1 as standard enthalpies relative to 298.15 K ($H^\circ - H_{298}^\circ$). Table 1 also shows the percent deviation between the experimental and smoothed values. Smoothed values are given in the "Discussion" section.

TABLE 1. - Experimental relative enthalpies of $V_2O_5(c, l)$

T, K	$H^\circ - H_{298}^\circ$, kcal/mol	Deviation, pct	Run	T, K	$H^\circ - H_{298}^\circ$, kcal/mol	Deviation, pct	Run
404.7	3.506	-0.02	1	¹ ,2950.1	37.742	Nap	17
511.4	7.368	-.04	2	2951.0	40.816	-0.01	15
604.4	10.938	.07	3	2951.9	40.870	.02	14
705.2	14.933	-.03	4	2952.9	40.912	.01	12
804.0	18.974	-.02	5	2955.4	41.014	-.01	9
854.3	21.072	.02	11	971.3	41.734	.00	8
903.7	23.141	.01	6	1,022.9	44.054	.00	10
¹ 925.8	24.133	Nap	7	1,101.0	47.563	.00	13
^{1,2} 949.0	37.531	Nap	16				

Nap Not applicable.

¹Onset of early melting; not considered in smooth-curve-fitting process.

² V_2O_5 was melted at 961 K for 0.5 h before temperature was lowered to value shown.

DISCUSSION

Relative enthalpy measurements were smoothed using a curve-fitting computer program developed by Justice (9). In this process, the high-temperature data were smoothly merged with the low-temperature data of Sukhovei (4). The fitting process used polynomials to derive the smooth thermodynamic values shown in table 2 at selected temperature intervals. The tabulated values are listed to three decimals to maintain internal consistency among the values, even though the experimental precision does not warrant this exactness. The smooth enthalpies of table 2 are estimated to have an absolute uncertainty of ± 0.3 pct. The standard deviation of the experimental enthalpies from the smooth values was small at 0.03 pct. Polynomials from the computer program were also used to derive smooth values of relative enthalpies at the temperatures of the experimental measurements in order to calculate the deviations shown in table 1. The average deviation of the measurements was low at 0.02 pct.

Measurements were stopped at 1,101 K because the capsule was slightly bulged. This pressure could have been caused by adsorbed gases as well as by a slight oxygen pressure due to the decomposition of V_2O_5 . The decomposition is negligible at the maximum temperature used for the measurements in this investigation

according to the data reported by Pan-kratz (10). X-ray powder diffraction analysis of the V_2O_5 removed from the capsule after completion of enthalpy determinations yielded the same pattern as that of the starting substance.

The relative enthalpies of V_2O_5 showed no irregularities in thermal behavior from 405 K until the melting point at 951 K. In measurements (described below) to determine the melting point, the V_2O_5 was liquefied at about 961 K, and this temperature was maintained for a minimum of 0.5 h before gradually being lowered for enthalpy measurements within 5 deg of the melting point. At 949.0 and 950.1 K, the V_2O_5 was partially melted and the measurements lay along the isothermal transition line between the smooth curves for the solid and liquid V_2O_5 . Measurements made at 951.0, 951.9, 952.9, and 955.4 K were found to lie on the liquid curve. Thus, a sharp melting point was determined at 951 K, with $\Delta H_m^\circ = 15.690$ kcal/mol for the standard enthalpy of melting. These values are compared to those reported by other investigators in table 3.

Enthalpy measurements conducted by other investigators were scattered and diverged from each other. Cook (1) made determinations with a 99.90-pct-pure sample in a copper-block calorimeter between 372 and 1,513 K. Slyusar (2)

TABLE 2. - High-temperature thermodynamic properties of V_2O_5 (c, ℓ)

T, K	cal/(mol·K)			$H^\circ - H_{298}^\circ$, kcal/mol
	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	
298.15	30.500	31.140	31.140	0
300	30.600	31.329	31.141	.057
350	32.959	36.238	31.523	1.650
400	34.684	40.757	32.399	3.343
450	36.060	44.924	33.562	5.113
500	37.197	48.784	34.894	6.945
550	38.161	52.376	36.322	8.830
600	38.989	55.733	37.801	10.759
650	39.705	58.882	39.303	12.727
700	40.325	61.848	40.808	14.728
750	40.861	64.649	42.305	16.758
800	41.319	67.301	43.785	18.813
850	41.704	69.818	45.243	20.889
900	42.022	72.211	46.675	22.982
950	42.274	74.490	48.080	25.090
¹ 951	42.278	74.535	48.108	25.132
951	44.940	91.033	48.108	40.822
1,000	44.940	93.291	50.267	43.024
1,050	44.940	95.483	54.368	45.271
1,100	44.940	97.574	54.376	47.518
1,150	(44.940)	(99.572)	(56.298)	(49.765)
1,200	(44.940)	(101.484)	(58.141)	(52.012)
1,250	(44.940)	(103.319)	(59.912)	(54.259)
1,300	(44.940)	(105.081)	(61.615)	(56.506)
1,350	(44.940)	(106.777)	(63.257)	(58.753)
1,400	(44.940)	(108.412)	(64.840)	(61.000)
1,450	(44.940)	(109.989)	(66.370)	(63.247)
1,500	(44.940)	(111.512)	(67.850)	(65.494)

¹Melting point.

NOTE.--Values in parentheses are extrapolations.

TABLE 3. - Melting points and heats of fusion of V_2O_5

Investigator	Melting point, K	ΔH_m° , kcal/mol	Method
Ferrante ¹	951	15.690	Copper-block calorimeter.
Slyusar (2).....	952 ± 5	16.013	Aluminum-block calorimeter.
Cook (1).....	943	15.560	Copper-block calorimeter.
Kohlmüller (11).....	937.9 $\pm .05$	14.5	Thermal analysis.
Pantony (12).....	951.12	13.8	Cryoscopic.
Murphy (13).....	963	ND	Differential thermal analysis.
Holtzberg (14).....	947 ± 5	ND	Thermal analysis.
Illarionov (15).....	945	ND	Differential thermal analysis.

ND No data.

¹Present investigation.

reported a purity of 99.96 pct for V_2O_5 used with an aluminum-block calorimeter from 577 to 1,095 K. In the present investigation, measurements were conducted with a 99.97-pct-pure sample in a copper-block calorimeter between 405 and 1,101 K. Enthalpies measured by Cook were higher than those of Slyusar by 6.9 pct at 500 K and 2.7 pct at 1,000 K. Cook's data were higher than those of the present investigation by 6.6 pct at 500 K and 1.3 pct for the liquid phase. Slyusar's enthalpy values were lower than the present investigation by 1.6 pct at 700 K and 1.4 pct at 1,000 K.

The smoothed enthalpies presented in tabular form are given below in simplified algebraic forms to better meet the needs of various users. The equations were derived from the smooth enthalpies of table 2 by Kelley's method (16). Because these equations contain six or fewer digits in a maximum of four terms, they give less precise enthalpies than the tabulated values calculated from the polynomials. However, the polynomials are not given because they can have up to 10 terms, with each term having 17 digits, and rounding of these numbers results in significant differences from the precise smooth values given in tabular form. The simplified equations derived by Kelley's method are obviously more convenient to use than the polynomials. The equations have been widely adopted as the standard form for the algebraic representation of high-temperature enthalpies because they give an adequate fit of the values without introducing undue complexity. The equations

are expressed in kilocalories per mole and are given below, with the temperature range of validity and the average deviation from the smoothed data shown in parentheses after each equation:

$$\begin{aligned} H^\circ - H_{298}^\circ &= 36.135 \times 10^{-3}T \\ &+ 3.886 \times 10^{-6}T^2 + 7.069 \\ &\times 10^2T^{-1} - 13.490 \\ &(298-951 \text{ K}; 0.1 \text{ pct}). \end{aligned}$$

$$\Delta H_{951}^\circ = 15.690.$$

$$\begin{aligned} H^\circ - H_{298}^\circ &= 44.940 \times 10^{-3}T - 1.916 \\ &(951-1,500 \text{ K}; <0.01 \text{ pct}). \end{aligned}$$

Standard enthalpies of formation (ΔH_f°), Gibbs energies of formation (ΔG_f°), and logarithms to the base 10 of the equilibrium constants of formation ($\log K_f$) were calculated as functions of temperature for V_2O_5 by combining relative enthalpies from the present investigation with auxiliary data from the literature. The results of these calculations are listed in table 4. For V_2O_5 , ΔH_f° was obtained from Wagman (17) and S_{298}° from Sukhovei (4). The data for $V(c)$ and $O_2(g)$ were taken from Chase (18-19). Since the heat capacity of the liquid was found to be constant for the temperature range in these measurements, this constant value was used to extrapolate to 1,500 K for the values given in tables 2 and 4.

TABLE 4. - Formation data for $2V(c, l) + 2.5 O_2(g) = V_2O_5(c, l)$

T, K	kcal/mol		Log Kf	T, K	kcal/mol		Log Kf
	ΔH_f°	ΔG_f°			ΔH_f°	ΔG_f°	
298.15	-370.600	-339.234	248.662	951	-366.625	-272.671	62.662
300	-370.598	-339.038	246.986	951	-350.935	-272.671	62.662
400	-370.313	-328.555	179.512	1,000	-350.451	-268.651	58.713
500	-369.810	-318.170	139.070	1,100	-349.510	-260.515	51.759
600	-369.184	-307.897	112.150	1,200	-348.635	-252.462	45.979
700	-368.488	-297.739	92.957	1,300	-347.823	-244.481	41.100
800	-367.752	-287.684	78.590	1,400	-347.079	-236.562	36.928
900	-367.004	-277.718	67.438	1,500	-346.400	-228.691	33.320

¹Melting point of V_2O_5 .

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